

THE USE OF INFRARED SPECTROSCOPY TO STUDY
SURFACE GROUPS AND ADSORBED SPECIES ON CATALYSTS

By Michael R. Basila

Gulf Research & Development Company
Pittsburgh, Pennsylvania 15230

INTRODUCTION In recent years the application of spectroscopic techniques to problems in surface chemistry and catalysis has been growing at an ever-increasing rate. The most popular technique has been infrared followed by nuclear magnetic resonance and electron spin resonance.

Infrared techniques are most useful in surface functional group identification and (through the use of adsorbed molecules as probes) in studying the nature of the active sites for adsorption and reaction. In some cases it has been possible to obtain mechanistic information concerning the nature of intermediates in simple reactions such as the decomposition of formic acid over supported and unsupported metal catalysts (1).

As an illustrative example of the use of infrared techniques in studying the behavior of surface functional groups and the utilization of molecular probes to characterize active surface sites, a review of our studies of the surface of silica-alumina will be given. Here, use was made of nitrogen containing molecules -- pyridine and ammonia -- as probes to characterize the surface acid sites.

SURFACE GROUPS ON SILICA-ALUMINA In Fig. 1 the spectrum of a highly dehydrated silica-alumina (25 wt.% Al_2O_3) is given. The band at 3745 cm^{-1} is due to the OH stretching vibration in surface hydroxyl groups. The bands at 1975, 1866 and 1633 cm^{-1} are overtone and combination lattice vibrations (2). There is also a weak band at 1394 cm^{-1} which is due to an unidentified surface group, possibly a surface impurity. The 3745 cm^{-1} band has been assigned to the OH stretching vibration in hydroxyl groups attached to surface silicon atoms (2). This assignment was made on the basis of similarities in the frequency, band shape and other properties with the surface hydroxyls on silica. It has been confirmed by nuclear magnetic resonance measurements (3). The presence of a single surface hydroxyl group type is rather surprising. A number of workers (4) have observed three to five OH stretching bands due to isolated (non-hydrogen bonded) surface hydroxyl groups on alumina, while only one band at 3750 cm^{-1} is observed on silica (5). The results for silica-alumina suggest that there are no alumina-like areas on the surface or conversely, that the aluminum ions are distributed evenly throughout the lattice. We have looked at other commercial silica-aluminas ($\text{Al}_2\text{O}_3 \leq 25\text{ wt.}\%$) and all have only a single surface hydroxyl type (attached to surface silicon atoms). Other workers have made similar observations (6a) however there have been several cases where the presence of alumina-like surface hydroxyl groups have been reported in addition to the silica-like groups (6b).

SURFACE ACID SITES Use has been made of ammonia as a molecular probe to study surface acidity on alumina and silica-alumina catalysts by a number of workers (7). Pyridine on the other hand has only been used in a few studies (8). Pyridine offers the advantage that one can distinguish unequivocally between coordinately bonded (LPY), protonated (BPY), and hydrogen bonded (HPY) adsorbed species (8). The bands that are used in making these distinctions are shown in Table I (8b).

TABLE I

BAND POSITIONS FOR COORDINATELY BONDED, PROTONATED
AND HYDROGEN-BONDED PYRIDINE ADSORBED ON SILICA-ALUMINA*

Species	Type	LPY (cm ⁻¹)	BPY (cm ⁻¹)	HPY (cm ⁻¹)
8a	✓CC(N)	1620	1638	1614
8b	✓CC(N)	1577	1620	1593
19a	✓CC(N)	1490	1490	1490
19b	✓CC(N)	1450	1545	1438

*LPY = coordinately bonded pyridine (chemisorbed)

BPY = protonated pyridine (chemisorbed)

HPY = hydrogen bonded pyridine (physically adsorbed)

Chemisorbed NH_3 exhibits two bands that can be used to distinguish between the coordinately bonded and protonated species. The position of these bands are at 1620 (LNH_3) and 1432 cm^{-1} (NH_4^+), respectively (7, 9). However, the (physically adsorbed) hydrogen-bonded species (PNH_3) cannot be distinguished from LNH_3 which introduces some uncertainty in the estimation of Lewis/Bronsted acid site ratios (9).

Figs. 2 and 3 are spectra of pyridine and ammonia adsorbed on silica-alumina. An expression for calculating the ratio of Lewis to Bronsted acid sites on the surface of silica-alumina using the 1490 and 1450 cm^{-1} bands of LPY and BPY has been developed (10).

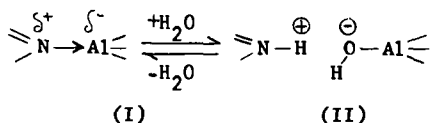
$$\frac{[\text{LPY}]}{[\text{BPY}]} = \frac{1.5 A_{1450}}{A_{1490} - 0.25 A_{1450}} ; A = \text{peak absorbance}$$

The band at 1545 cm^{-1} cannot be used directly in conjunction with the 1450 cm^{-1} band because it has a much smaller absorption coefficient and the ratios are usually considerably greater than 1. The use of the 1490 cm^{-1} band is convenient because for LPY and BPY it has different absorption coefficients with $\epsilon_{\text{BPY}}/\epsilon_{\text{LPY}} = 6$ (10).

The bands at 1620 and 1432 cm^{-1} of chemisorbed ammonia can be used directly to estimate the Lewis/Bronsted acid site ratio. The relative absorption coefficients are: $\epsilon_{1432}/\epsilon_{1620} = 7$ (9). By these two methods it has been determined that one out of every five (NH_3 , (9)) to 7 (PY, (10)) molecules that are chemisorbed are adsorbed as the protonated species for the silica-alumina which was studied comparatively. Other silica-aluminas have different Lewis/Bronsted acid site ratios (10) which is to be expected since the relative amounts of alumina and methods of preparation vary over considerable ranges.

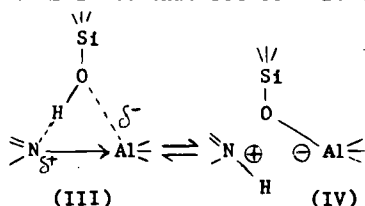
EFFECT OF WATER ON SURFACE ACIDITY More detailed studies of the adsorption of pyridine and ammonia on silica-alumina have exposed some rather interesting behavior. When H_2O is adsorbed on chemisorbed pyridine (8) or ammonia (10) containing samples most of the LPY (LNH_3) is converted to BPY (NH_4^+) (Figs. 2b, c). However, this reaction is reversible and the spectrum returns to the original upon evacuation (Fig. 2d). During this experiment H_2O does not displace pyridine since no pyridine is removed and no band due to HPY is observed. If pyridine is added to chemisorbed H_2O , the same spectrum results but the water is removed by subsequent evacuation (8b). Hence, it appears that the H_2O molecules interact with the chemisorbed LPY and a proton transfer occurs without displacement of LPY.

It is difficult to rationalize the nature of this interaction between water and chemisorbed pyridine or ammonia. It is important to note that pyridine and water in solution do not interact to form pyridinium ion but merely engage in hydrogen bonding interactions (11). The formation of BPY therefore must result from activation of one or both of the components by the surface. The results suggest that the nitrogen containing base stays on the primary acid site and the water participates in a secondary interaction. Presumably adsorption of pyridine to form LPY occurs by an electron transfer interaction from the lone electron pair on the N atom to a trigonal surface aluminum atom leading to a surface complex of the type (I).



In the presence of water, the electron transfer from N to surface Al may be essentially complete if a hydrogen atom from the water is transferred to the LPY and the OH radical migrates to the aluminum atom to give a complex of type (II). The same result would occur if a proton was transferred to the pyridine and the hydroxyl ion to the trigonal aluminum atom. In either case the pyridinium ion would then be held on the surface in an ion pair with ($\geq \text{AlOH}$)⁻. The only difficulty with this model is that the nitrogen base is apparently strongly held during this interaction (8b) since it does not desorb upon evacuation whereas the pyridinium ion should have some surface mobility. The real situation most likely involves an equilibrium between (I) and (II), however, the data suggest that it is strongly displaced to the right since most of the LPY can be converted to BPY. It should be noted that there are no data available to indicate whether the added H₂O molecules are in a 1:1 ratio with the number of LPY molecules. If the ratio were higher, the equilibrium would be pushed toward the right.

SURFACE ACIDITY MODEL These results have led us to postulate (8b) that all of the acidic sites on silica-alumina are of the Lewis or electron acceptor type and that Bronsted type acidity results from a secondary interaction between the molecule chemisorbed on the primary Lewis type site and an adjacent SiOH group. This interaction is pictured as similar to that between water and chemisorbed LPY.



This model's chief advantage is that it allows the rationalization of extensive data in the literature which heretofore has been taken as evidence that silica-alumina has predominantly Lewis type sites or conversely predominantly Bronsted sites. It suggests that a proton is available if needed mechanistically such as to form a classical carbonium ion from an olefin, but is not necessarily involved in all acid-catalyzed reactions that proceed over silica-alumina (9).

Spectroscopic evidence supporting this model will now be considered. In Fig. 4 a plot of the concentration of chemisorbed NH_4^+ versus total ammonia adsorbed is given. As would be expected the slope decreases as the total amount of ammonia adsorbed increases. The initial slope is 0.25 which indicates that initially one

out of every five ammonia molecules is chemisorbed as NH_4^+ . Fig. 5 is a plot of the concentration of isolated (non-hydrogen bonded) surface hydroxyls versus the total amount of ammonia adsorbed. For analysis the smooth curve is broken into two linear segments. Note that the intersection point coincides with the point (Fig. 4) where the increase in (NH_4^+) as total ammonia adsorbed increases begins to flatten out. The inverse slope of the low coverage linear segment in Fig. 5 is 5.5 ± 0.5 and that of the high coverage linear segment is 0.98 ± 0.09 . Hence, at low coverage one out of every five or six chemisorbed ammonia molecules is hydrogen bonded to a surface hydroxyl group. At high coverage every adsorbed ammonia is hydrogen bonded to a surface hydroxyl group, which is typical of the physical adsorption of ammonia on silica gel (no acidic sites). It is evident from these results that the high coverage segment corresponds to physical adsorption and the low coverage segment to chemisorption. The curvature near the transition point is a result of both processes occurring simultaneously.

According to the predictions of the model $[\text{NH}_4^+] \leq [\text{OH}]$ bonded, that is the number of chemisorbed ammonia molecules which are involved in "hydrogen-bonding" interactions with surface hydroxyl groups should be greater than or equal to the concentration of chemisorbed NH_4^+ . The results in Figs. 4 and 5 (at low surface coverage) are that one in five ammonia molecules is chemisorbed as NH_4^+ and one in five or six is hydrogen bonded to a surface hydroxyl group, in good agreement with the prediction. Furthermore, it is predicted that hydroxyl groups involved in proton transfer interactions with chemisorbed ammonia molecules should not exhibit an OH stretching band, hence at low surface coverage where chemisorption predominates the intensity of the 3050 cm^{-1} band (due to the hydrogen-bonded OH stretching) should increase at a very much lower rate than at high coverage where physical adsorption predominates. This behavior is evident in Fig. 6 where the peak absorbance of the 3745 cm^{-1} band is plotted versus that of the 3050 cm^{-1} band. This evidence is not conclusive however because the OH groups in a non-proton transfer interaction with chemisorbed molecules may have a different peak frequency and absorption coefficient than those involved in a normal hydrogen-bonding interaction (9).

Additional supporting evidence for the proposed model is shown in Fig. 7. In this experiment the silica-alumina was poisoned by impregnation with potassium acetate followed by calcination. The presence of alkali metals in acidic catalysts is known to poison carbonium ion reactions (13). Fig. 7a shows that the band due to BPY at 1545 cm^{-1} is absent, hence poisoning with potassium ions eliminates Bronsted type acidity. It has been shown (8b) that the strength of the acidic sites is markedly decreased when silica-alumina is poisoned by the addition of potassium. The hydroxyl groups are little effected. When water is adsorbed on the pyridine containing surface the LPY species are converted to BPY (Fig. 7b). Hence the added potassium ions do not prevent the conversion of LPY to BPY by adsorbed water. This result is quite surprising. It eliminates the surface species $(\geq \text{AlOH})^-\text{H}^+$ as the source of inherent Bronsted acidity on a fresh silica-alumina surface. If this species were present the K^+ ions would exchange with the H^+ ions and render the sites completely inactive. The fact that water can still convert LPY to BPY suggests that even though the degree of activation of pyridine by the acidic site is decreased (8b) the protonation reaction can still proceed if the proton donor can get close enough.

This behavior can be rationalized in terms of our model as follows and hence is taken as indirect supporting evidence. Since the reactions of the LPY-acid site complex and the adjacent OH are geometrically fixed a decrease in the degree of activation of LPY can prevent the transfer of a proton. However, water molecules are mobile and can come in very close proximity to the complex to effect proton transfer.

SUMMARY The results discussed above demonstrate that infrared spectroscopic techniques can provide details of surface chemistry and the nature of surface functional groups. Spectroscopic techniques do not provide the panacea for all catalytic problems, however. They sometimes raise more questions than they answer. It can be concluded that they will (and do) constitute an important tool for the catalytic chemist. They are most effective when used in conjunction with other techniques such as gravimetric adsorption measurements (used for example to obtain surface concentrations in Figs. 4 and 5) and isotope exchange techniques.

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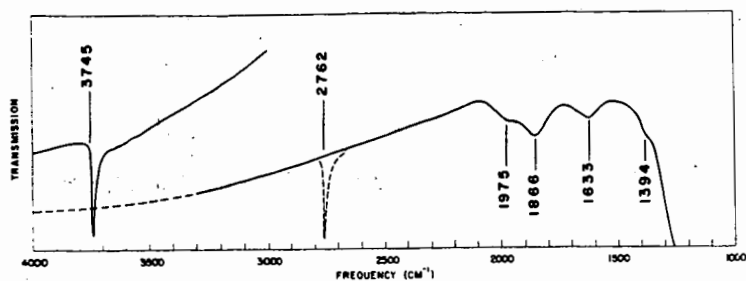


Fig. 1. Silica-alumina dehydrated at 500°C. The dashed lines indicate the spectrum of deuterated silica-alumina.



Fig. 2. Dual adsorption of pyridine and H_2O on silica-alumina. (a) SA exposed to pyridine at 17 mm. and 150°C for 1 hr. followed by evacuation at 150°C for 16 hr. (b) Exposure to H_2O at 15 mm. and 150°C for 1 hr. followed by evacuation at 150°C for 1 hr. (c) Exposure to H_2O at 15 mm. and 25°C for 1 hr. followed by evacuation for 1 hr. at 25°C. (d) Evacuation for 16 hr. at 150°C.

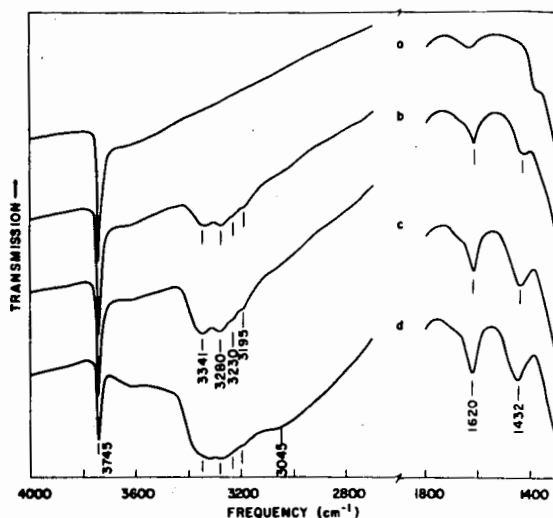


Fig. 3 (a) SA calcined 16 hours in O_2 at 500°C, evacuated 5 hours at 500°C. (b) Exposed to 10 mm NH_3 for 1 hour at 150°C, evacuated 1 hour at 150°C. (c) Subsequently exposed to 10 mm NH_3 for 1 hour at 25°C, evacuated for 1 hour at 25°C. (d) Subsequently exposed to 10 mm NH_3 for 1 hour, no evacuation. Very weak bands due to gaseous NH_3 have been subtracted.

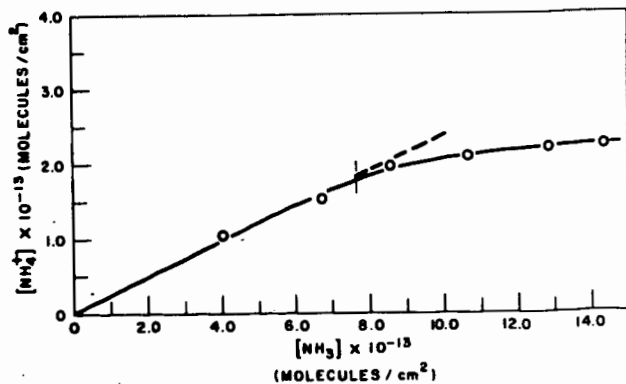


Fig. 4. A comparison of the concentrations of NH_3 and NH_4^+ adsorbed on SA as the total amount of ammonia adsorbed increases. $[\text{NH}_3]$ is the sum of $[\text{PNH}_3]$ and $[\text{LNH}_3]$. The vertical line denotes the point of straight line intersection in Fig. 5.

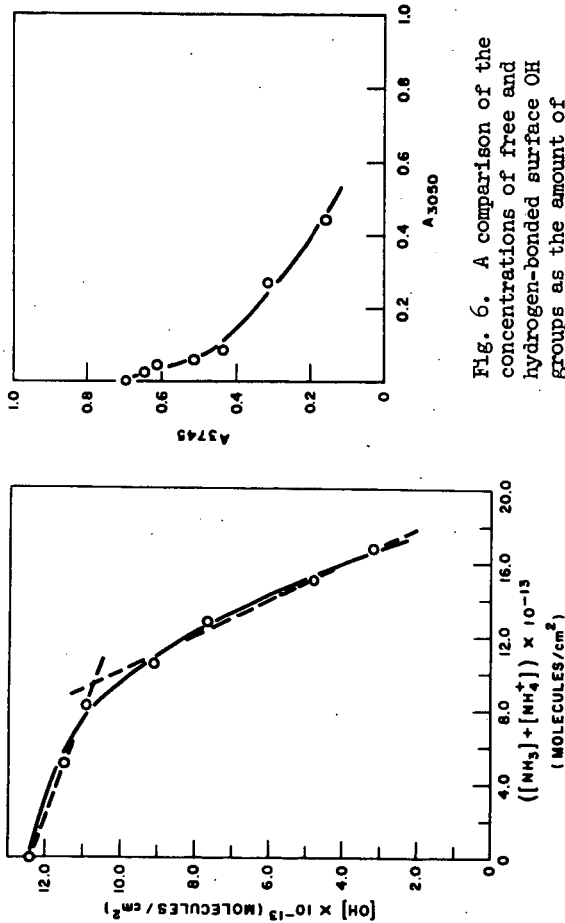


Fig. 5. The concentration of non-hydrogen bonded surface OH groups vs the total amount of ammonia adsorbed on SA-NH₃. is the sum of PNH₃ and LN₃.

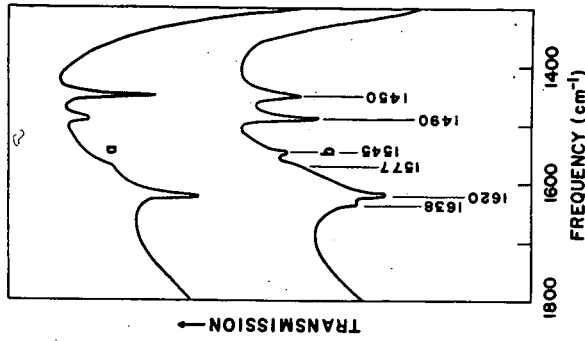


Fig. 6. A comparison of the concentrations of free and hydrogen-bonded surface OH groups as the amount of ammonia adsorbed increases. The values of A are the peak absorbancies of the characteristic bands.

Fig. 7. Dual adsorption of pyridine and H₂O on K-poisoned silica-alumina. (a) KSA exposed to pyridine at 17 mm. and 150°C for 1 hr. followed by evacuation for 16 hr. at 150°C. (b) Exposed to H₂O at 15 mm. and 150°C for 1 hr. followed by evacuation for 1 hr. at 150°C.